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⑤4固型着色材

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明 細 書

発明の名称

固型着色材

特許請求の範囲

塩化ビニルポリエチレン、ロジンと多価アルコールのエステル、前記エステルと相容するアルキッド樹脂、沸点110～200℃の炭化水素系溶剤、グリコールエーテルの低級脂肪酸エステルより選ばれた1種又は2種以上の溶剤、および顔料よりなる固型着色材。

発明の詳細な説明

本発明はクレヨンまたは口紅等の固型着色材に関する。特に筆記あるいは塗布すれば速かに乾燥して強靭な着色皮膜をつくるので、マーカーとして利用でき、あるいは筆先の細密又は小さい面の塗装等に便利に使用できる固型着色材に関する。

従来ペイント、ラッカー等の塗料は主として顔料と展着剤を混練した液状又はペースト状物が用いられており、これ等は塗布に際して溶剤で希釈したり、あるいは筆や刷毛のような塗布用具を必要とし、使用後筆や刷毛を溶剤等で丁寧に洗っておくなどのわずらわしさがあつた。使用簡便のためスプレー式塗料が市販されているが構造複雑で高価であつた。またフエルトペンのように筆や刷毛が必要でなく、容易にマーキングや小面積の塗装に便利なものも普及しているが、これ等は主として耐光性に劣る有機染料を着色料として使用しているので長期間屋外に放置すると色があせてしまい、かつ耐熱性が弱い欠点を有しており、更に染料を使用した場合はその上にペイント等を塗装すると下の染料が溶け出てくる欠点を有している。且つ染料では白色のものを作ることが出来ず、白色は顔料によつてのみ得られフエルトペンに於ては通常の構造では顔料インキを透用する事は非常に困難であり、市販の白のマーカーは顔料を分散したインキを使用しており、アルミ管などにインキを充填してスプリング機構で弁を開閉して繊維束等のペン先にインキを導出させるようにしているが、これ等に用いられている顔料インキは長期

過たつと顔料が沈降して揮発成と分離するのでアルミ管の中に玉球などを入れてこれを振つて攪拌せねばならず、また使用に際してはペン先を何度も押したりする必要があり、インキの出方が一定でなく、濃度も一定になりにくい不便さがあつた。最近有機溶剤とこれに相溶する樹脂及び着色材にベンジリデンソルビトールのようなゲル化剤を使用して塗料を固型化した固型マーカーが開発されているが、この組成のものではゲル破壊硬度が50kg／cdを超えると筆記時の抵抗が大きくなり筆記困難となる。即ち滑かに筆記できる程度のものは軟かすぎて折損しやすく、硬くて折損しないものは書きづらい欠点がある。しかし本発明では破壊強度が２００kg／cd以上となつても筆記の滑らかなものが得られる特徴がある。

本発明による固型着色材はマーカーまたはペイントとして使用するに際し、回転式繰出容器などに装填してあれば、キャップをとりすぐ書き出すことが出来て、筆や刷毛が不用であり、布紙も従来もペン先を押す必要もなく、常に一定の濃度、好き味で筆記出来る大きな長所を有するもので、プラスチック、金属、ガラス、木材、紙、等の面に、或は粗面、平滑面、さらに、油または水で僅かに濡れた面でも容易に筆記出来て、且つ溶剤が揮発した後は、これ等の面に強く密着してなお適度の柔軟性を有し、耐候性、耐摩擦性にすぐれた塗膜を得る事の出来るものである。

本発明の必須成分の第１は乳化型ポリエチレンである。近来ポリエチレン系のプラスチックは安価で耐水，耐薬品性にすぐれ、成型性もよいなどの特徴のために広く利用されているが、乳化型ポリエチレンは比較的低分子量のポリエチレンに酸化処理を施し、部分的にカルボン酸基やカルボニル基を導入したものでアルカリ性では水に乳化分散させる事も出来て、通常のポリエチレンに比して有機溶剤樹脂類との相溶性、混和性をもち、特に炭化水素系溶剤およびグリコールエーテルの脂肪酸エステルとは軟化点以上に於て均一に混和し、冷却すれば強固なゲルを形成する特質を有する。このゲルを紙や金属面などにクレヨンの様に塗布し、乾燥させると溶剤のみが揮発し、あとに乳化型ポリエチレンの塗膜が残るのであるが、乳化型ポリエチレンのみでは密着性も弱く、爪で指などでこすつても、引掻いても剥落しやすい。故に溶剤揮発後の塗膜に密着性を与えるために、乳化型ポリエチレンにこれと相溶性を有するおよび柔軟性を与え乍らも密着性を増すアルキッドロジンと多価アルコールのエステル樹脂（以下エステル樹脂と記す）樹脂類を添加すればきわめて密着性、耐摩擦性にすぐれた塗膜を得ることが出来るのである。

塗膜に柔軟性を与えるためには可塑剤のようなものも有効ではあるが、二塩基酸エステル等を主とする一般の可塑剤は乳化型ポリエチレンと相溶性が悪く、低分子のポリオレフインなどは相溶性は良くともゲル化が悪くなり、実際に可塑タックが多く残存でない。即ち、本発明に於いては、密着性を与えるためには乳化型ポリエチレンと相溶性がよく、強靭な塗膜を与え、且つ乾りやすく、耐摩擦性もよく、溶剤揮発後常温で塗布、成型性

も良好であるところのエステル樹脂を添加することが最適であると判断される。更に塗膜に或る程度の柔軟性を与えながら密着性を良好に保ち、空気酸化あるいは重合によつて更に強固な塗膜を与えるためにエステル樹脂と相溶性を有し、乳化型ポリエチレンとも親和性を有するものとしてアルキッド樹脂類の添加が好適である事を見出した。上記３成分に適度の硬度，延伸性を与えるために溶剤が添加される。かくして得たゲルに着色料としての油料を加え、流し込み、押出等の成型法で所望形状に成型すれば本発明の固型着色材が得られ、回転式或はチック式容器などに装填すれば前記のように良好なマーカーまたはペイントとして使用する事が出来るのである。

本発明で用いられる乳化型ポリエチレンワックスとは、分子内にカルボキシル基を有する低分子量のポリエチレンであり、その内ＪＩＳＫ ２５３０の測定法による針入度が３以下の範囲であつて酸価が約10以上軟化点 100℃以上の範囲のものが好ましく使用できる。針入度が上記範囲を外れる場

合には筆記性が悪くなり、又、酸価が上記範囲を外れる場合には他の成分との混和が困難となる。好ましく使用できる乳化型ポリエチレンワックスとしては、例えば、商標名「ＡＣポリエチレン＃３９２」、「ＡＣポリエチレン＃６８０」、「ＡＣポリエチレン＃６９０」（以上、アライドケミカル社製）、「三井ハイワックス２１０２Ｅ」、「三井ハイワックス４０５３Ｅ」（以上、三井石油化学工業社製）、「パリコＥ２０２０」（米国ペトライト社製）として市販されているもの等を挙げることができる。乳化型ポリエチレンワックスは、クレヨン全量の約２０～６０重量％、好ましくは３０～５０重量％が用いられる。使用量が、約60重量％を超えるとクレヨンが硬くなり過ぎて筆記性が低下する傾向を生じ、~~又その為に筆記圧が高くなり、結果的に紙面に多量に付着するもので結果として消去性も低下もする~~。又、約２０重量％以下では、クレヨンが軟かくなり、筆記時の抵抗が大となる。一般に固型着色剤を細く成型し、細書用に供する場合には高軟化点のものを多く用いてエチレンもエステル樹脂も共に耐熱性にやや劣る欠点を有するので、塗膜に或る程度の柔軟性を与え、溶剤揮発後は空気酸化、内部架橋などにより経時的に更に強靭な塗膜を与えるアルキッド樹脂類の使用が良好である事を見出したのであるが、アルキッド樹脂類は概してエステル樹脂類と相溶性がよく、殊に乳化型ポリエチレンとは相溶性が悪い場合でもロジンエステル樹脂に対し、過量とならない範囲に於て使用すれば良好な混和性を有し、安定したゲルを得る事が出来るのである。アルキッド樹脂類としては乾性油変性アルキッド樹脂、スチレン化アルキッド樹脂、アクリル変性アルキッド樹脂、油変性ウレタン樹脂等いずれも過量にならない範囲で用いる事が出来る。一般にアルキッド樹脂類は石油系溶剤に溶解された状態で市販されているがこれ等溶剤の含有量、種類を考慮して使用すれば本発明の着色鉛筆芯を得るのにはなんら支障はなく、使用量は樹脂により、相溶性の程度により差はあるが着色剤全量に対し固型分で３～１５％、好しくは５～１０％が用いられ、又エステル樹脂に対して固型分で１０～５０％程度用いることが出来、好しくは１５～30％がよい。少いと効果が小さく、多すぎると相溶性のバランスがくずれなお指触乾燥時間が長くなる。

本発明に用いられる着色料としての顔料は一般に絵具塗料等に用いられているものはすべて使用可能であるが、顔料を完全に溶解するためには、１４０℃以上にも加熱が必要な場合もあるので耐熱性のよい顔料が好ましく、酸化チタン、ベンガラ、カーボンブラック等の無機顔料は勿論好適であるが、有機顔料としてはフタロシアニンブルー、フタロシアニングリーン、キナクリドンマゼンタ、イエローアゾ系、インダスレン系のオレンジや赤の顔料などが有用であり、勿論耐溶剤性の良いものが望ましい。顔料の用いる量は色によつて大きな差がありすべて塗料、絵具などの書線の線が遮蔽出来るが平均的には全重量の１５～４０％程度が適当である。

有機溶剤は芳香族、脂肪族、脂環族を含む様に

水系溶剤の他にエステル，ケトン，エーテル，グリコールエーテル類等いずれも沸点が110°～200℃の範囲のものならばほとんどのものが使用可能であるが、乳化型ポリエチレンの軟化点以上の温度でこれを溶解し、且つ他成分樹脂をもよく溶解し、冷却時安定したゲルとなるものを検討した結果沸点110°～200℃の炭化水素系溶剤、グリコールエーテルの低級脂肪酸エステルのうち一種または之等以上が適当である事を見出した、即ちキシレン，エチルベンゼン，イソプロピルベンゼン，エチルシクロヘキサン，メチルエチルシクロヘキサン，イソプロピルシクロヘキサン，テトラリン，デカリン，ミネラルターペン，その他東永燃業製ソルベソソ，日本石油製ソルベント等の商品名で呼ばれている石油系溶剤および各種有機溶剤のうちエチルセロソルブアセテート，イソプロピルセロソルブアセテート，メトキシブタノールアセテート，ブチルセロソルブアセテート，メチルセロソルブプロピオネート，エチルセロソルブプロピオネートなどのグリコールエーテル低級脂肪酸エステルが好適であり、全重量の10～40％が好ましくは15～25％が用いられる。溶剤が多いとゲルが軟かくなりすぎて、少いとかたくなりすぎてつきのびが悪くなり、用いる乳化型ポリエチレンの種類量をはじめ他の配合材の種類，量によつても異るが10～20％が望ましい。

次に本発明の熱可塑着色材を製造する実施例を記し、本発明を明らかにする。以下部とあるは重量％を指す。

実施例1

ACポリエチレン＊392	8％
ACポリエチレン＊680	24％
エステルガムEG－H（徳島精油製　水添ロジングリセリンエステル樹脂）	18％
ペツコゾールJ544（大日本インキ化学工業製　乾性油アルキド樹脂キシレン50％）	10％
キシレン	15％
ルチル型酸化チタン	25％

上記原料を（総量10kg）を15ℓ加熱電伴釜に入れて可逆冷却管をつけて140℃に加熱し、全体がよく溶融して来た時点で撹拌を開始し、1000rpm/minの高速撹拌を30分間継続し樹脂類を溶解させ、顔料を分散させて後130℃にて回転式容器に流し込み、放冷して褐色の熱可塑着色材を得た。このものは熱可塑白色マーカーとして充分の硬さと着色力を有し、且つ書き味もよくガラス面に塗記して20℃，60％湿度に2分後には充分指触乾燥する事が確められた。

実施例2～5

実施例1に準じて熱可塑着色材を得た。この場合、混合温度，吸管温度，指触乾燥時間およびゲル破壊強度が各々相異するので次に表示する。

実施例	混合温度 ℃	吸管温度 ℃	指触乾燥時間 分	ゲル破壊強度 kg/cm²	色
1	140	130	2	98	白
2	120	120	2	82	青
3	140	130	3	130	黄
4	120	120	3	110	赤
5	140	130	2	160	白
6	130	120	4	114	黄

実施例2

ACポリエチレン＊680	16％
三井ハイワックス＊405 3E	22％
エステルガムPE－H（徳島精油製　水添ロジンペンタエリスリトールエステル樹脂）	20％
トクシノールR102－5（徳島精油　スチレン化アルキッドーソルベツソ50％を含む）	8％
エチルセロソルブアセテート	6％
キシロール	8％
ルチル型チタン	15％
シアニンブル4920（大日精化製）	5％

実施例3

ACポリエチレン＊392	10％
三井ハイワックス2102E	32％
ハリマツク135G（播磨化成工業製　ロジングリセリンエステル軟化点135）	12％
ペツコゾール130J（日本ラ沙ホールド製ロジン変性アルキッドーキシロール50％）	8％
メトキシブタノールアセテート	15％
タルク	20％
三菱カーボンMA100（三菱化成製）	5％

実施例4

パリコE2020 44%
(USA ペトロライト社製乳化型ポリエチレン)

エステルガムPE-H 14%

スチレゾール4250 6%

(大日本インキ化学工業製スチレン化アルキッド,キシロール 50%)

イソプロピルセロソルブアセテート 14%

ルチル型酸化チタン 6%

タルク 8%

セイカファーストレッド1975 8%
(大日精化製 赤色顔料)

実施例5

ACポリエチレン#392 8%

〃 680 30%

エステルガムPE 16%
(徳島精油製ロジンペンタエリスリトールエステル)
軟化点95～105 Av10～20

トクシノールAA2 7%
(徳島精油 アクリル変性アルキッド,キシロール 50%)

イソプロピルシクロヘキサン 15%

ルチル型酸化チタン 24%

実施例6

三井ハイワックス4053E 40%

エステルガムPE 18%

オレスターF77-60MS 7%
(油変性ポリウレタン樹脂 三井東圧化学製)

ブチルセロフルブアセテート 8%

デカリン (デカハイドロナフタリン) 8%

ルチル型酸化チタン 12%

イルガジンバイオレットGRLT 7%
(チバガイギー社製)

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SOLID COLORING MATERIAL
[Kokei chakushokuzai]

Akio Hatakenaka

UNITED STATES PATENT AND TRADEMARK OFFICE
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TITLE	(54): SOLID COLORING MATERIAL
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Title of the Invention

Solid Coloring Material

Claim

Solid coloring material comprised of emulsifying type polyethylene, ester of rosin and polyvalent alcohol, alkyd resin compatible with the above-mentioned ester, one or more types of solvent selected from among hydrocarbon solvents that have a boiling point of 110 to 200°C and lower aliphatic esters of glycol ethers, and pigment.

3. Detailed Specifications

[Field of Industrial Use]

This invention pertains to a solid coloring material for crayon or lipstick. More particularly, this invention pertains to a solid coloring material that, because it dries quickly when written or painted, can be used conveniently as a marker or in applications such as touching up painted surfaces or painting small surfaces.

Previous paints such as paint or lacquer have used liquids or pastes blended primarily of pigment and resin solution. When these are applied, dilution by solvent or use of an application tool such as a writing brush or paint brush is required, and after use, effort must be expended such as washing the writing brush or paint brush clean with solvent. To simplify use, spray type paints are marketed, but these are complicated in structure and expensive. Also, products such as felt pens that do not require a writing brush or paint brush are used widely and are convenient for easy marking or painting small surfaces, but because these primarily use organic dyes with inferior light resistance as

coloring agents, these have the drawback that colors fade when left outdoors for a long time and they also have poor heat resistance. Furthermore, when dyes are used, these have the drawback that when paint or other coating is applied over these, the dye underneath bleeds. Moreover, white paint cannot be created using dyes, and white color can be obtained only by pigments. In the case of felt pens, it is extremely difficult to apply pigment ink in a standard structure, and white markers that are marketed use ink in which pigment is dispersed. In some designs, an aluminum tube or the like is filled with ink and ink is conducted to a pen tip such as a fiber bundle by opening and closing a valve by a spring mechanism. However, because the pigment in the pigment ink used in these settles over time and causes the resin solution to separate, steel balls or the like must be placed in the aluminum tube and agitated, and the pen tip also must be pressed several times before using. In addition, ink does not issue steadily, it is difficult to maintain a constant concentration, and pens are inconvenient to use. Recently, solid type markers have been developed in which paint is solidified by using organic solvent and a gelling agent such as benzylidene sorbitol in resin that is compatible with the organic solvent and coloring material. However, if gel breakdown hardness in this composition exceeds 50 kg/cm^2, resistance during writing increases and writing becomes difficult. That is, this composition has the drawback that materials that are soft enough that writing can proceed smoothly break too easily, and materials that are hard enough not to break are difficult to use in writing. However, this invention has the special characteristic that smooth writing can be obtained even when

breakdown strength is 200 kg/cm^2 or greater.

When solid coloring material in accordance with this invention is used in markers or paint, it has the great advantages that when housed in a container such as a lipstick dispenser, paint can be used immediately upon removing the cap without requiring a writing brush or paint brush, there is no need to dilute, agitate, or press the pen tip, and writing can be produced at a concentration that is always constant. Therefore, writing can be achieved easily on surfaces such as plastics, metals, glass, wood, or paper, on rough or smooth surfaces, and even on surfaces that have been moistened by a small amount of oil or water. In addition, after solvent vaporizes, paint adheres tightly to surfaces such as these and, moreover, has appropriate softness, and paint film can be obtained that has superior weather resistance and abrasion resistance.

The first essential component of this invention is emulsifying type polyethylene. Recently, polyethylene plastics have become widely used for their low cost and characteristics such as superior chemical resistance and good moldability, but because emulsifying type polyethylene is made by performing oxidation treatment on relatively low molecular weight polyethylene and partially introducing carboxylic acid groups or carbonyl groups, it becomes alkaline and can be emulsified and dispersed in water. As a result, compared to standard polyethylene, it is compatible and miscible with organic solvent resins, and in particular, has the characteristic that it becomes a hard gel when evenly blended with hydrocarbon solvents and glycol ether aliphatic acid esters at or above the softening temperature, then cooled. When this gel

is applied using a crayon or the like on a surface such as paper or metal, then dried, only the solvent vaporizes and a film of emulsifying type polyethylene remains afterward. However, if only emulsifying type polyethylene is used, this film has poor adhesion and easily peels off even when lightly wiped by a finger or scratched. Therefore, when, to impart adhesion to paint film after solvent vaporizes, an ester resin of alkyd rosin and polyvalent alcohol (hereafter abbreviated as "ester resin") that has compatibility with this polyethylene and increases adhesion even while it imparts softness and alkyd resins that increase adhesion even while they impart softness are added to emulsifying type polyethylene, paint film can be obtained that has extremely superior adhesion and abrasion resistance.

To impart softness to paint film, compounds such as plasticizers are effective, but the main general plasticizers such as dibasic acid esters have poor compatibility with emulsifying type polyethylene. Although compounds such as low molecular weight polyolefins have good compatibility, they become soft in gels, often cause so-called tacking in paint film, and are not appropriate. That is, in this invention, to increase adhesion, it was judged that it is ideal to add ester resin that has good compatibility with emulsifying type polyethylene, imparts a hard paint film, is easy to apply, has good dispersibility with pigment, has low viscosity when melted, and has satisfactory agitation and molding properties. Furthermore, it was discovered that it is ideal to add alkyd resins that have satisfactory adhesion while imparting a certain degree of softness to paint film, have compatibility with ester resin for imparting still further hardness to paint film by oxidizing in

air or polymerizing, and have affinity with emulsifying type polyethylene. To impart appropriate hardness and extension to the three components described above, additives are added. When pigment is added as coloring material to the gel obtained in this way and this is molded to the desired shape by a molding method such as casting or extruding, the solid coloring material of this invention is obtained, and when housed in a lipstick type or tic type container or the like, this can be used as a satisfactory marker or paint as described above.

The emulsifying type polyethylene wax used in this invention is a low molecular weight polyethylene that has carboxyl groups in its molecular structure. Among these, polyethylene waxes can be used by preference that have penetration in the range of 3 or less, acid value of 10 or more, and softening point in the range of 100°C or higher according to the measurement methods stipulated in JIS K 2530. When penetration falls outside of the range given above, writing properties are impaired, and when the acid value falls outside of the range given above, blending with other components becomes difficult. Emulsifying type polyethylene waxes that can be used by preference include, for example, polyethylenes marketed under the trade names of "AC polyethylene #392," "AC polyethylene #680," and "AC polyethylene #690" (the above are manufactured by Allied Chemical Co.), "Mitsui High Wax 2102E" and "Mitsui High Wax 4053E" (the above are manufactured by Mitsui Petrochemical Industries Co.), and "Paliko E2020" (manufactured by U.S. Petrolite Co.). Emulsifying type polyethylene waxes are used at approximately 20 to 60 wt%, and preferably 30 to 50 wt% of the total amount of crayon. When the amount used exceeds approximately 60 wt%, the

crayon becomes too hard and writing properties tend to be reduced. Also, at less than approximately 20 wt%, the crayon becomes soft and presents great resistance during writing. Generally, when solid coloring material is finely molded and used for fine writing, a component may be used that has a high softening point to create a hard gel, and when thick coloring material is created, a component may be used that has a low softening point to make the crayon softer. However, it is preferred that the intended hardness by obtained by selecting the appropriate amount for blending.

Ester resins generally are used to impart tackiness to products such as paints, printing inks, or adhesives, and ester resins of rosin or hardened rosin and polyvalent alcohols—that is, alcohols such as ethylene glycol, diethylene glycol, glycerin, or pentaerythritol—can be used in the solid coloring material of this invention. Because use of ester resin that has a low enough softening point produces tackiness in paint film, ester resins with a softening point of 80°C or higher are preferred. In terms of molecular weight ratio, this may be used at a content of 10 to 30%, and preferably 15 to 25% of the total amount of solid coloring material and 30 to 80%, and ideally 40 to 60% of emulsifying type polyethylene. Also, when pigment is added to emulsifying type polyethylene and ester resin alone, paint film becomes too hard and becomes brittle, and produces fissures when impacted or bent and peels off when scratched or otherwise abraded. Also, because both emulsifying type polyethylene and ester resin also are slightly inferior in heat resistance, it was discovered that satisfactory results are obtained by blending in alkyd resins that impart a certain degree of

softness to paint film and create a harder paint film over time through a process such as oxidation in air or cross-linking after solvent vaporizes. Moreover, alkyd resins generally have good compatibility with ester resins, and even should they have poor compatibility with emulsifying type polyethylene, when blended within a range that is not excessive relative to the rosin ester resin, they show satisfactory compatibility and a stabilized gel can be obtained. As alkyd resins, resins such as drying oil modified alkyd resins, styrenated alkyd resins, acrylic modified alkyd resins, or oil modified urethane resins can be used so long as the amount used is not excessive. Generally, alkyd resins are marketed dissolved in petroleum solvents, but so long as the type and content of these solvents is checked before use, there is no objection to using these to obtain the solid coloring material of this invention. The amount used depends on the type and degree of compatibility, but alkyd resins can be used at 3 to 15%, and preferably 5 to 10% solid parts per total amount of solid coloring material, and at about 10 to 50%, and preferably 15 to 30% solid parts per total amount of ester resin. When less is used, the effect is less, while when more is used, the balance of compatibility is broken. Moreover, the length of time until dry to the touch is increased.

As the pigments used as coloring material in this invention, generally all pigments used in artist paints or the like can be used. However, because dissolving base ingredients fully sometimes requires heating to 140°C or higher, heat-resistant pigments are preferred. Inorganic pigments such as titanium oxide, rouge, or carbon black of course are ideal, but organic pigments such as phthalocyanine blue,

phthalocyanine green, quinacridone [as transliterated] yellow, or indanthrene orange or red also are useful. Needless to say, pigments that have good compatibility are preferred. The amount of pigment used differs greatly by color, and the line of common sense for paints, artist paints, or the like can be applied. On average, however, a pigment content of about 15 to 40% of the total is appropriate.

As the organic solvent, in addition to hydrocarbon solvents including aliphatic and alicyclic solvents, nearly all organic solvents such as esters, ketones, ethers, or glycol ethers can be used so long as the boiling point is in a range of 110 to 200°C. However, in results of tests in which these were dissolved at the temperature of the softening point of emulsifying type polyethylene, other component resins were added and well dissolved, and a stable gel was obtained when cooled, it was discovered that one or more types of hydrocarbon solvents that have a boiling point of 110 to 200°C or lower aliphatic acid esters of glycol ethers are most appropriate. Specifically, xylene, ethyl benzene, isopropyl benzene, methyl cyclohexane, methyl ethyl cyclohexane, isopropyl cyclohexane, tetralin, decalin, mineral turpentine, and also petroleum solvents known by trade names such as Sorvesin by Toei Industries or Solvesso by Nippon Oil Co.; and among the various organic solvents, glycol ether lower aliphatic acid esters such as ethyl cellosolve acetate, isopropyl cellosolve acetate, methoxybutanol acetate, butyl cellosolve acetate, methyl cellosolve propionate, or ethyl cellosolve propionate are ideal. These are used at a content of 10 to 40%, and preferably 15 to 25% of the total. When there is too much solvent, gel becomes too soft, while when there is too little solvent,

gel becomes too hard and appearance suffers. Starting with the type and amount of emulsifying type polyethylene, this differs depending on the type and amount of this and other ingredients, but solvent content of 10 to 20% is preferred.

Next, this invention is clarified by citing embodiments of manufacture of the solid coloring material of this invention. In the following, numbers marked by "%" indicate wt%.

Embodiment 1

AC polyethylene #392	8%
AC polyethylene #680	24%
ester gum EG-H (Tokushima Oil Refining, hydrogenated rosin glycerin ester resin)	18%
Bekko Sol J544 (Dainippon Ink and Chemicals, drying oil alkyd resin, xylene: 50%)	10%
xylene	15%
rutile titanium oxide	25%

The ingredients listed above (total weight: 10 kg) were placed in a 15 ℓ heat agitating kiln, a reversible cooling tube was attached, and the kiln was heated to 140°C. At the point when all ingredients were well dissolved, agitation was started and high-speed agitation at 1000 rpm was continued for 30 minutes. After resins had dissolved and pigment was dispersed, this was cast in a lipstick type container at 130°C, then cooled to obtain bar-shaped solid coloring material. This material had adequate hardness and coloration as a solid white marker, and moreover, had good writing properties. By writing on a glass surface, after 2 minutes at 20°C and 60% humidity, it was confirmed that material was

adequately dry to the touch.

Embodiments 2 to 5

Solid coloring materials were obtained following Embodiment 1. Because blending temperature, molding temperature, time until dry to the touch, and gel breakdown hardness in these cases showed slight differences, these properties are displayed in the following table:

Embodiment	Blending Temperature °C	Molding Temperature °C	Time Until Dry to the Touch min	Gel Breakdown Hardness kg/cm^2	Color
1	140	130	2	98	white
2	120	120	2	82	blue
3	140	130	3	130	black
4	120	120	3	110	red
5	140	130	2	160	white
6	130	120	4	114	purple

Embodiment 2

AC polyethylene #680	16%
Mitsui High Wax 4053E	22%
ester gum PE-H (Tokushima Oil Refining, hydrogenated rosin pentaerythritol ester resin)	20%
Tokushinol S102-5 (Tokushima Oil Refining, styrenated alkyd resin, contains 50% Solvesso)	8%
ethyl cellosolve acetate	6%
xylol	8%
rutile titanium	15%
cyanine blue 4920 (Dainippon Ink and Chemicals)	5%

Embodiment 3

AC polyethylene #392	10%
Mitsui High Wax 2102E	32%

Harimac 135G 12%
(Harima Chemical Industries, rosin glycerin ester, softening point: 135°C)

Bekko Sol 1303 6%
(Nippon Raka Hold Co., rosin-modified alkyd, xylol: 50%)

methoxybutanol acetate 15%

talc 20%

Mitsubishi carbon MA 100 5%
(Mitsubishi Chemical Industries Co.)

Embodiment 4

Valco E2020 44%
(USA Petrolite Co., emulsifying type polyethylene)

ester gum PE-H 14%

Styresol 4250 6%
(Dainippon Ink and Chemicals, styrenated alkyd, xylol: 50%)

isopropyl cellosolve acetate 14%

rutile titanium 6%

talc 8%

Seika Facetread 1975 8%
(Dainichi Seika Co., red pigment)

Embodiment 5

AC polyethylene #392 8%

" #680 30%

ester gum PE 16%
(Tokushima Oil Refining, rosin pentaerythritol ester, softening point: 95 to 105°C, Av: 10 to 20)

Tokushinol AA2 7%
(Tokushima Oil Refining, acrylic-modified alkyd, xylol: 50%)

isopropyl cyclohexane 15%

rutile titanium oxide 24%

Embodiment 6

Mitsui High Wax 4053E	40%
ester gum PE	18%
Olester F77-60MS (oil-modified polyurethane resin, Mitsui Toatsu Chemicals Co.)	7%
butyl cellosolve acetate	8%
decalin (decahydronaphthalene)	8%
rutile titanium oxide	12%
Irgazin violet red 6RLT (Chiba-Geigy Co.)	7%